

# Cocatalysts for Metal-Catalyzed Olefin Polymerization: Activators, Activation Processes, and Structure–Activity Relationships

Eugene You-Xian Chen\*

The Dow Chemical Company, Catalysis R&D, Midland, Michigan 48674

Tobin J. Marks\*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received September 13, 1999

## Contents

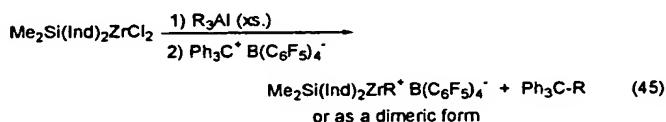
I. Introduction	1391	3. Coordination by Neutral Alkyl Metal Complexes	1417
II. Activators	1393	4. Strong Anion Coordination via Fluoride or Hydride Bridges	1418
A. Aluminum Alkyls	1393	5. $\eta^n$ - $\pi$ Arene Coordination	1418
B. MAO	1394	6. Multicenter M–Si–C Interactions	1419
1. General Structural Features of MAO	1394	7. Alkenyl/Dienyl Coordination	1419
2. Modified MAOs	1394	C. Kinetics of Ion-Pair Dissociation/Reorganization	1419
3. Pentafluorophenyl-Substituted MAO	1395	D. Thermodynamics of Catalyst Activation	1421
C. Perfluoroaryl Boranes	1395	E. Activity and Stereoselectivity Aspects	1422
D. Fluoroarylalanes	1397	1. Catalyst–Cocatalyst Structure Match	1422
E. Trityl and Ammonium Borate and Aluminate Salts	1398	2. Correlations of Ion-Pair Energetics, Dynamics, and Polymerization Activity	1423
F. Cocatalysts Containing Non-Group 13 Elements	1400	3. Polymerization Stereospecificity	1424
G. Supported Organometallic Activators	1401	F. Deactivation and Stabilization in Solution	1426
1. Supported MAO	1401	1. Deactivation Processes	1426
2. Silica-Bound $\equiv\text{Si}=\text{O}-\text{B}(\text{C}_6\text{F}_5)_3^-$ Anions	1401	2. Stabilization of Ion Pairs in Solution	1428
3. Supported $\text{PhNMe}_2\text{H}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ and Borate Anions	1402	V. Concluding Remarks	1429
4. Superacidic Solid Brønsted Acids	1402	VI. Acknowledgment	1430
III. Activation Processes	1403	VII. References and Notes	1430
A. Oxidative and Abstractive Cleavage of M–R Bonds by Charged Reagents	1403		
B. Protonolysis of M–R Bonds	1404		
C. Alkyl/Hydride Abstraction by Neutral Strong Lewis Acids	1405		
1. Bis-Cp Type Group 4 Metallocene Activation	1406		
2. Mono-Cp Group 4 Complexes	1409		
3. Non-Cp Group 4 Metal Complexes	1411		
4. Other Metal Complexes	1412		
D. Ligand Exchange and Subsequent Alkyl/Halide Abstraction for Activating Metal Halide Complexes	1413		
E. One-Electron Oxidation and Reduction	1414		
IV. Catalyst–Cocatalyst Structure–Activity Relationships	1415		
A. Lewis Acidity of Fluoroaryl Boranes	1415		
B. Solid-State Structural Features of the Cation–Anion Ion Pairs	1416		
1. $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ Anion Coordination via Agostic Interactions	1416		
2. Weak Anion Contacts via Fluorine Atoms	1417		

## I. Introduction

One of the most exciting developments in the areas of catalysis, organometallic chemistry, and polymer science in recent years has been the intense exploration and commercialization of new polymerization technologies based on single-site and metallocene coordination olefin polymerization catalysts.<sup>1</sup> The vast number of specifically designed/synthesized transition metal complexes (catalyst precursors) and main-group organometallic compounds (cocatalysts) allows unprecedented control over polymer microstructure, the generation of new polymer architectures, and the development of new polymerization reactions. Commercialization of new generations of single-site and metallocene catalyst-based technologies has provided the multibillion pound per year polyolefins industry with the ability to deliver a wide range of new and innovative olefin-based polymers having improved properties.<sup>2–4</sup> The intense industrial activity in the field and the challenges to our basic understanding that have come to light have in turn

$\alpha$ -olefins,<sup>228</sup> and tridentate pyridine diimine Fe(II) and Co(II) dihalides for linear, high-density polyethylene<sup>229,230</sup> and moderately isotactic polypropylene via a 2,1-insertion mechanism.<sup>231,232</sup>

A ternary system that consists of a zirconocene dichloride, a trialkyl aluminum, and  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  has been developed by Chien et al.<sup>233</sup> for ethylene and propylene polymerizations with superb activity. The use of excess of  $\text{R}_3\text{Al}$  serves both to alkylate the dichloride precursor as well as to scavenge  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , and other protic impurities in the system.<sup>234</sup> The entire activation process can be perceived as the initial in-situ alkylation of the zirconocene dichloride by the alkylaluminum, followed by subsequent oxidative cleavage of a Zr–R bond by  $\text{Ph}_3\text{C}^+$  (eq 45). This

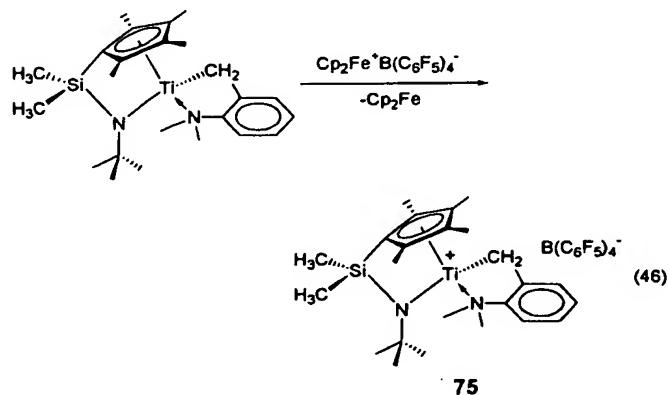


convenient approach avoids using zirconocene di-alkyls as catalyst precursors; however, caution must be taken regarding the quantity of trialkylaluminum needed to optimize the catalytic efficiency. Although an excess of such species can serve as a scavenger, it could also deactivate the system and thus lower the efficiency. For example, TMA has been found to react with  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  to form a series of exchange products<sup>184</sup> as well as to "intercept" metallocenium cations to form heterodinuclear complexes.<sup>137</sup> Unlike MAO-activated catalytic systems, the optimum activity of this system is very sensitive to the polymerization temperature.<sup>233-236</sup> Typically, the highest activity obtained from  $\text{L}_2\text{ZrR}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  species generated in situ is when the polymerization is carried out from 0 to -20 °C. The noncoordinating features of the anion and the low olefin insertion barrier for this system allows high efficiencies to be achieved at low polymerization temperatures—as low as -60 °C. On the other hand, there is an activity loss in high-temperature polymerizations. Choice of aluminum alkyls also sometimes affects the stereospecificity of propylene polymerization<sup>237</sup> and chain transfer reactions.<sup>238</sup> It was reported that propylene polymerization catalyzed by a  $[\text{ArN}(\text{CH}_2)_3\text{NAr}]\text{TiCl}_2$  ( $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ) complex, when activated with TMA (or TEA)/ $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ , produces atactic polypropylene. However, when TIBA/  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  is employed as the activator, propylene polymerization affords a mixture of atactic and isotactic polypropylene.<sup>237</sup> The isotactic index (II; defined as weight fraction of isotactic polymer in refluxing heptane; hexane was used to fractionate the crude polymer in this example) depended strongly on the polymerization temperature, and the highest isotacticity (II = 78.9%,  $T_m = 129.2$  °C) was achieved at a polymerization temperature of ~40 °C.

### **E. One-Electron Oxidation and Reduction**

One-electron oxidation of the stable Ti(III) complex  $(C_5Me_5)_2Ti(CH_3)$  by  $Ag^+[BPh_4^-]$  in THF yields  $(C_5Me_5)_2Ti(CH_3)(THF)^+$ .<sup>239</sup> Similar oxidation of  $[Cp_2ZrCl]_2$  by  $Ag^+$  was used earlier to prepare  $Cp_2ZrCl(L)^+X^-$  ( $X^-$

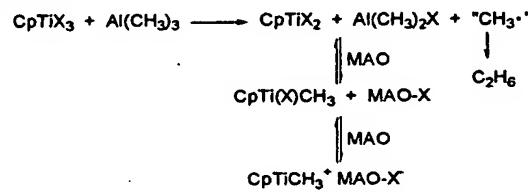
=  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ ) salts.<sup>240</sup> Furthermore, (CGC)Ti(III) catalyst precursors can be activated with ferrocenium tetrakis(pentafluorophenyl)borate and oxidized to cationic Ti(IV) species **75**, which is a very active olefin polymerization catalyst (eq 46).<sup>241</sup> Another disclosure



by the Dow group suggests that active catalysts can alternatively be prepared by electrochemical oxidation of Ti(III) and Ti(IV) catalyst precursors, obviating the need for chemical oxidizing agents such as ferrocenium salts.<sup>242</sup>

Mono-Cp (single-ring)-type titanium complexes  $\text{Cp}^*\text{TiX}_3$  ( $\text{X} = \text{Cl}, \text{CH}_3, \text{CH}_2\text{Ph}, \text{BuO}$ ) when activated with MAO,  $\text{B}(\text{C}_6\text{F}_5)_3$ , or  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  catalyze rapid syndiospecific styrene polymerization to produce highly syndiotactic polystyrene.<sup>243-248</sup> The activation mechanism and the true active species responsible for the syndiospecific enchainment of styrene have been subjects of considerable debate. A popular hypothesis is that the true active species is actually a  $\text{Ti(III)}^+$  complex, formed by reduction of the initial  $\text{Ti(IV)}$  species by MAO,  $\text{AlR}_3$ , or by some other mechanism.<sup>249-251</sup> Reduction is probably caused by the free trimethylaluminum contained in MAO, since aluminum alkyls are more effective reducing agents than alumoxanes (Scheme 17).<sup>243</sup> Although

**Scheme 17**



ESR studies have confirmed the formation of such  $\text{Ti(III)}^+$  species, present in significant amounts (the exact percentage varies with ligands and catalyst aging time) in the activated solution mixture, the activation mechanism and the function of other species formed are yet to be determined. Other experiments appear to support this hypothesis, since isolated and characterized  $\text{Cp}'\text{M(IV)}\text{Me}_2^+$  ( $\text{M} = \text{Zr}$ ,  $\text{Hf}$ ) complexes catalyze only aspecific styrene polymerization to yield atactic polystyrene.<sup>73</sup> However, the isolable  $\text{Ti(III)}$  complex  $\text{Cp}'\text{Ti}(\text{OMe})_2$  produces highly syndiotactic polystyrene after activation with either MAO or TIBA/ $\text{PhMe}_2\text{NH}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  and even exhibits greater catalytic activity than  $\text{Cp}'\text{Ti}(\text{OMe})_3/\text{MAO}$ .<sup>252</sup>